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Invited Paper

The scope of the ZnO growth

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ABSTRACT

The main ZnO physical properties are reviewed and some of them compared to those of GaN. As a result of these attractive properties, the various applications it could be thought of for ZnO are summarized. A critical review is then proposed of the different techniques used for the growth of bulk ZnO crystals and of ZnO epitaxial films. The results are discussed from the assessment of their structural and electrical properties. The key issue of *p*-type doping is finally discussed in the light of the most recent results.

Keywords : ZnO physical properties, ZnO applications, ZnO bulk growth, ZnO epitaxial growth, ZnO doping

1. INTRODUCTION

ZnO can be considered as an 'old' semiconductor. It has been studied and used for a long time in a wide range of applications such as piezoelectric transducers, optical waveguides, acoustooptic media, conductive gas sensors, transparent conductive electrodes, varistors. It is now reactivated and becomes again topical for applications related not only to its optoelectronic possibilities in the UV range but also to its piezoelectric properties to develop SAW filters to be integrated in future analog circuits for portable electronic for which there is a strong need.

It is worth knowing that ZnO occupies already an enviable place in the industrial market. Tens of thousands tons of ZnO powder are industrially produced each year! They are used in the rubber industry as vulcanisation activator (~36 %), in the industry of ceramics as a flux (~26 %), in the chemical industry (desulphuration of gases, fabrication of stearates, phosphates..etc) (~20 %), as trace elements in the animal food (~12 %), in the paints (~3 %; 50 % in 1961!). The last ~3 % are used for different applications, in electronics (ferrites, varistors), ends of matches, pharmaceutic industry (fungicidal properties of ZnO for skin-problems, trace elements ..etc.).

ZnO powder is produced from the combustion of vapours coming from the distillation of metallic zinc, according to the so-called French process, or dry process. Using vapours coming from fractionated distillation, extra-pure oxide powders are produced, as illustrated from the chemical analysis data of two kinds of powder produced by two different companies:

- Quality 'pharmacy B', produced by Union Minière : Pb<20 ppm, Cd<10 ppm, Fe<5 ppm, Cu<1 ppm.
- Quality 'colloidal', produced by Silar SA : Pb<20 ppm, Cd<30 ppm, Fe<5 ppm, Cu<2 ppm, Mn<2 ppm.

The grain size can change according to the variety considered.

After summing up the main physical properties of ZnO, which is now attracting tremendous interest, the recent growth aspects of the compound, not only for making bulk crystals, but also epitaxial layers, will be addressed and critically reviewed. The doping issue will be also discussed in the light of the most recent results.

2. ZnO PHYSICAL PROPERTIES

If the field of wide band gap semiconductors has been clearly dominated by the nitride compounds during the last five years, the recent first International Workshop on ZnO (Dayton October 7-8 1999) and the Ninth International Conference on II-VI Compounds (Kyoto November 1-5 1999) have shown that the trend of the ten coming years could turn in favor of the semiconductor oxides because of their attractive physical properties.

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In most of the applications aimed at by the nitrides, the oxides demonstrate fundamental advantages.

- ZnO has a band gap of 3.37 eV @ RT
- It presents a unique combination of piezoelectric (e_{33} = 1.2 C/m^2, among the highest values of all semiconductors), conducting, thermal (thermal conductivity of 0.54 Wcm^{-1}K^{-1}, to compare with 0.5, for example, for GaAs) and optical properties
- It has the largest exciton binding energy of all II-VI and III-V semiconductors, 60 meV, allowing excitonic stimulated emission up to 550 K, as already demonstrated[1]
- *P*-type conductivity, which remains a problematical issue for GaN, has been now reported for ZnO, as will be shown further, and paves the way to realization of junctions.
- Unlike GaN, high quality substrates are now produced by a variety of techniques, sublimation (40 mm diameter, by Eagle Picher), hydrothermal growth, vertical Bridgman under pressure, chemical vapor transport. This means that the ZnO homoepitaxy is now possible. As a result, layers of improved physical properties ought to be obtained, and the cleavage issue for making lasers, particularly difficult for GaN layers deposited on sapphire, should be made easier
- The ternary system CdO-ZnO-MgO covers a larger band gap range than nitrides with a smaller variation of the lattice parameter [3.24 to 3.26 Å from ZnCdO (2.8 eV) to ZnMgO (4 eV)]
- The ZnO drift mobility saturates at higher fields and at higher values than the GaN ones which is attractive for high frequency devices[2]
- ZnO is more radiation resistant (up to 2 MeV, 1.2×10^{17} electrons/cm^{-2}) than GaN
- ZnO UV detectors show very low dark current; their spectral response showing a maximum at the optimum wavelength of 350nm
- ZnO shows a strong two-photon absorption with high damage thresholds, which is very attractive for optical power limiting devices
- ZnO has a large shear modulus. The shear modulus has been identified to be a key material signature expressing the stability of the crystal[3]. The shear modulus of ZnO has been recently calculated by Vérié[4] and found to be ~45.5 Gpa. By comparison, the shear modulus of ZnSe has been estimated to be 18.35, 32.60 for GaAs, 51.37 for Si.
- ZnO has finally the same crystallographic structure as GaN, with a lattice mismatch < 1.8%, and can then act as alternative substrate for GaN.

Beside GaN,

- ZnO is more radiation hard
- shows higher drift mobilities at higher electric fields
- has a higher exciton binding energy
- could be easier to convert to *p*-type, at higher concentrations
- its homoepitaxy is possible
- its film growth deposition temperatures are smaller (~ 400 °C)
- it is easier to cleave
- the CdO-ZnO-MgO system shows great potentialities, covering an energy range going from 2.8 eV to 4 eV with a weak variation of the lattice parameter
- zinc is more abundant, less expansive than gallium, and no toxic

Owing to these attractive assets, many applications can be thought of for ZnO. In addition to now classical applications (piezoelectric transducers, optical waveguides, acoustooptic media, conductive gas sensors, transparent conductive electrodes) the future perspectives of ZnO are hetero- and homo-epitaxial *p*/*n* junctions; LED's and lasers in blue and UV region; UV detectors for solar blind applications; high field electron devices; high power, high temperature electronics ; future wireless communication systems at frequencies beyond 5 GHz ; variable optoelectronic grating ; optical power limiting devices for high peak power pulses ; large diameter high quality substrates for GaN. It could furthermore be thought of also as an efficient scintillator.

Furthermore, a ferromagnetic phase transition, induced by a gas of electrons and holes, is expected from a theoretical work[5] in the ZnMnO alloys at a Curie temperature higher than room temperature. This could lead to new physics and to the realization of devices based on the control of the spin state (spin electronics or spintronics) like quantum computers.

3. ZnO BULK GROWTH

Roughly four techniques are presently used to grow bulk ZnO crystals.

- In spite of its very high melting point of ~ 1900 °C and of its high reactivity with any surrounding material but platinum, cm-sized ZnO crystals with rocking-curve FWHM of ~125 arcsec have been grown from the melt by the Bridgman method using Cermet's melt growth apparatus with water-cooled crucible under high oxygen pressure (50 atm)[6]. The perspective is to reach 2 inch diameter substrates.
- The hydrothermal method has been shown suitable for the growth of large ZnO crystals from $(OH)^-$ solutions at temperatures <500°C under high pressure (15 to 50 MPa) with a temperature difference $\Delta T \sim 3$ - 40K and a growth rate in the range 0.05-0.3 mm/day[7-10]. More recently, high quality ZnO crystals, as demonstrated by X-ray rocking curves in the 40 arcsec range and sharp PL peaks, have been grown hydrothermally at 355 °C with a ΔT of 10°C from NaOH/KOH solutions as the solvent, pressures of 18,000 to 22,000 psi (maximum pressure 1500 atm)[11]. The crystals present a dislocation density < 500 cm^{-2}, a X-ray double diffraction FWHM ~130 arcsec and carrier mobilities ~175 cm^2/Vs @ RT. The O and Zn surfaces of (0001) planes have been found to behave differently. GaN layers deposited at 750 °C on such substrates show DDX FWHM of 735 arcsec. Using a KOH/LiOH solvent, ZnO bulk single crystals about 10 mm in dimension have been grown at temperatures less than 400 °C at pressures ranging from 830 to 1110 MPa[12].

  The advantages of the hydrothermal technique are a low growth temperature, a ΔT close to 0 at liquid/solid interface, an 'easily scalable' technique, the reduction of most of the impurities from source (except Li, incorporated in the crystals at 1-20 ppm). The disadvantages are the presence of intermediate products, the slow growth rates (~10 mils per day), the inert liner needed, the occasional incorporation of OH and H_2O, the lithium incorporation. The goal is an increase in the crystal size as well.
- Large diameter (2-inch diameter) boules have been recently reported to be grown at Eagle Picher at 1000-1200 °C by seeded physical vapor transport (SPVT) in a nearly closed horizontal tube using H_2 as a carrier gas and a small amount of water to maintain the proper stoichiometry[13]. The crystals are seeded at full diameter ; the source/substrate distance is of about 3 inches ; the stoichiometry is controlled from the presence of a residual water pressure ; the growth rates are of about 40 µm per hour. The present diameter of the crystals is 40 mm ; the etch pit (dislocation) density is of about 10^4 cm^{-2} ; the X-ray double diffraction rocking curve FWHM is of about 40 arcsec, with some scattering indicating the presence of residual strains. GDMS analysis reveals the purest material ever done by Eagle Picher. The crystals are of n-type with $n \sim 8\times10^{16}$ cm^{-3} and $\mu \sim 150$-350 cm^2/Vs @ RT. The homoepitaxial growth of ZnO on such substrates has been achieved on <0001> Zn faces chemo-mechanically polished. The future goal is now the growth of 3 inch diameter substrates.

  Furthermore, residual water, present in H_2 or Ar, has been shown to act as a sublimation activator of the vapor phase transport of ZnO[14].
- Smaller crystals have been obtained by chemical vapour transport (CVT) in closed tubes using such chemical transport agents as HCl, Cl_2, NH_3, NH_4Cl, $HgCl_2$, H_2, Br_2, $ZnCl_2$ at source temperatures ranging from 800 to 1150°C and ΔT from 20 to 200°C[15-19]. Centimeter-size single crystals with rocking curve FWHM ~ 28 arc.sec have been recently obtained using C as a new transporting chemical agent[20].

Crystals of small size have been grown as well in open tube systems, either by oxidation of ZnI_2[21], ZnS, ZnSe[22], $ZnBr_2$[23] and Zn[24-26] or by hydrolysis of ZnF_2[27], $ZnCl_2$[28,29], ZnI_2[30]. The oxidation or hydrolysis character of the reaction can depend on the temperature range used for a same source. The temperature of the growth region ranges generally in such experiments from 900 to 1350°C.

Such solvents as PbF_2[31] and V_2O_5/P_2O_5 mixtures[32] have been used for the flux growth of ZnO crystals. Using PbF_2 as the solvent in sealed Pt crucibles, ZnO crystals have been grown by THM[33]. $PbCl_2$ has been found to be a very good solvent of ZnO as well, but showing also a great reactivity with any surrounding material but platinum[34]. The same authors have found the Zn-In alloys to be good solvents of ZnO without reactivity with silica.

4. ZnO EPITAXIAL FILM GROWTH

ZnO thin polycrystalline films dedicated to the 'traditional' applications of ZnO, as specified above, are classically deposited by such techniques as sputtering, chemical vapor deposition, chemical spraying, electron cyclotron resonance plasma sputtering, sol-gel deposition, ion-beam assisted deposition, pulsed laser deposition etc.

More recently homoepitaxial and heteroepitaxial ZnO films dedicated to the 'new' ZnO applications for optoelectronic devices have been grown by four techniques :

- Classical ZnO sputtering has been achieved on (0001) sapphire substrates[35]. A (0002) rocking-curve FWHM as low as 250 arcsec has been measured, but more generally of about 400 arcsec. The roughness was < 1nm (the best 0.1 nm). The resistivity ranged from 3 to 10^5 Ωcm depending on the growth and cooling conditions. Under low pressure (3-150 mTorr) sputtering, rocking-curve FWHM $\leq$1080 arcsec[36] has been measured on sapphire substrates. Epitaxial ZnO films have been grown on Si(111) substrates by rf magnetron sputtering using a GaN buffer layer deposited by the same technique[37]. The films show a crack-free morphology. RF magnetron sputtering has been used as well for the deposition of epitaxial ZnO films on diamond (111) planes at 260 °C[38] (smallest X-ray rocking-curve FWHM of 972 arcsec measured on the ZnO (0002) peak) and on $LiNbO_3$(0001)[39] substrates at 550 °C (rocking-curve FWHM for the ZnO (0002) reflection ~1650 arcsec). The same kind of result was obtained on non-cristalline substrates (alumina and silica) using a two-step method in which a thin ZnO buffer layer was first deposited by magnetron sputtering, the epitaxial films being then deposited by CVD technique[40].
- ZnO, ZnMgO and ZnO/GaN films have been grown on sapphire substrates by pulsed laser deposition by Vispute et al.[41,42]. The substrate temperature was 750 °C for ZnO/sapphire and 500-750 °C for ZnO/GaN/sapphire under an O_2 pressure of 10^{-5}-10^{-4} Torr. The measured EPDs and rocking-curve FWHM were respectively 10^{10}/cm^2 and ~ 612 arcsec on ZnO/sapphire and 10^8/cm^2 and 180 arcsec on ZnO/GaN. Epitaxial ZnO thin films showing a FWHM rocking-curve ~ 600 arcsec have been grown on sapphire substrates using ultra-violet pulsed laser deposition at temperatures higher than 400 °C by Cracium et al.[43].
- MOCVD, generally on sapphire substrates, is carried out with separate inlets of the precursors to avoid pre-reactions, with DEZn for Zn and O_2[44,45], O_2, N_2O or H_2O[46] (with or without plasma), CO_2[47,48] (with a plasma) or alcohol (butanol[49,50]) as oxidizers, and Ar, He or N_2 as the carrier gas, in the temperature range 350-650 °C
  - either in a horizontal reactor[49,50]
  - or in a vertical rotating disk reactor operated at low pressure with high speed rotation of the wafer carrier, with separated introduction of the precursors[44-46], sometimes through a multi-nozzle shower[46]. The possibility of obtaining both conductivity types, *n* and *p*, has been demonstrated using N_2O, NH_3 and N_2 (with and without plasma activation) for N doping[46].

  A very few significant characteristics of the MOCVD grown ZnO layers are given. Only a value of 1500 arcsec has been reported for the FWHM of the (0002) diffraction peak[48]. No electrical properties are reported for these MOCVD grown ZnO layers...
- MBE has been achieved by several groups for the growth of ZnO layers and related ternary alloys with Cd, Mg and Mn, according to two main variants :
  - Either laser-MBE (pulsed laser deposition, PLD, in ultra-high vacuum) on $ScAlMgO_4$ substrates[51] or on sapphire for ZnO[52] and ZnO/$Mg_xZn_{1-x}O$ quantum structures[53]
  - Or by plasma-assisted MBE[54-61], with variants like radical source MBE[62] (RS-MBE), electron cyclotron resonance assisted MBE[63] (ECR-assisted MBE), depending on the plasma cell used. ZnO films have been generally grown on sapphire substrates, using such buffer layers as MgO[54,58], GaN[55], or ZnS[56] and on Si[62]. Such heterostructures like $Mg_{0.2}Zn_{0.8}O$/ZnO/ $Mg_{0.2}Zn_{0.8}O$ and ZnO/ZnCdO/ZnO on sapphire (0001), $ScAlMgO_4$ (0001) (SCAM) and ZnO/GaN substrates have been also grown[64]. The growth temperature lies in the range 275-600 °C.

  More details than in the MOCVD case are given concerning the structural and electronic properties of the layers. The following rocking-curve FWHM have been reported : 216 arcsec[57], 378 arcsec[51], 576 arcsec[60], 1080 arcsec[59], 2016 arcsec[63] for ZnO directly deposited on Al_2O_3, but 39 arcsec[51] for ZnO(0002) on SCAM, and 13 arsec[58] using a MgO buffer layer on sapphire. The layers grown without doping are always of *n*-type, with a carrier concentration closely related to their crystallographic perfection : electron concentration of 1.87×10^{18} cm^{-3} associated with a mobility of 10 cm^2/Vs for ZnO layers grown on Si[61], but $n = 10^{15}$ cm^{-3}, $\mu \sim 100$ cm^2/Vs for ZnO layers deposited on SCAM[51] and $n = 2.1\times10^{16}$ cm^{-3}, $\mu \sim 98$ cm^2/Vs for ZnO layers deposited on MgO/Al_2O_3[58].
- Using Radical beam epitaxy (RBE), *n*-type, *p*-type ($p = 4\times10^{14}$ cm^{-3}, $\mu \sim 23$ cm^2/Vs) or semi-insulating ZnO films have been produced at temperatures within 150-950 °C by bombardment of singlet O($\downarrow\uparrow$) radicals extracted from an oxygen plasma, using a magnetic filter, on substrates of any Zn chalcogenide (ZnTe, ZnSe, ZnS, ZnO)[65]. No information about their structural properties.

5. DOPING

Whatever the growth method used, ZnO bulk crystals and films exhibit almost always strong *n*-type conductivity, with *n* lying generally in between 10^{17} and 10^{19} cm^{-3}. It has been long assumed that the dominant donor was a native defect. From a recent first-principle investigation[66], it has been demonstrated that none of the dominant native defects, zinc and oxygen vacancies and Zn_O antisites, has characteristics consistent with a high-concentration shallow donor. Furthermore, V_O has been identified from electron paramagnetic resonance studies as a deep donor[67]. Hydrogen or a complex native defect-hydrogen has been suggested to be responsible for the strong donor behavior[66]. We have analyzed by SIMS the residual concentration of hydrogen in ZnO bulk crystals grown by CVT using carbon as the chemical transport agent. Neither hydrogen nor residual carbon were found in these crystals which showed an electron concentration @ RT of $\sim 2\times10^{18}$ cm^{-3}. The assignment of the residual native shallow donor in ZnO to Zn_i, as proposed by Look et al.[68], remains the best hypothesis

The key issue for the ZnO and related alloys development remains *p*-type doping.

Minegishi et al.[69] reported for the first time the growth by chemical vapor deposition of *p*-type films realized by the simultaneous addition of NH_3 in the carrier hydrogen and excess Zn in the ZnO powder source. The RT hole concentration reached 1.5×10^{16} cm^{-3}, with $\mu \sim 12$ cm^2/Vs. But the resistivity remained too high (generally ~100 Ωcm) for making devices such as LEDs, and the results were poorly reproducible.

Later on, *p*-type electrical conduction has been achieved, according to a theoretical prediction[70], by Ga and N codoping of ZnO layers grown by pulsed laser deposition[71]. One sample only is reported to show an acceptor concentration of 4×10^{19} cm^{-3}, with a very poor mobility of 7×10^{-2} cm^2/Vs. The authors stress the fact that the *p*-type behavior seems to be very small and sensitive to experimental parameters.

A ZnO diode has been fabricated by using a laser-annealing doping technique to form a *p*-type ZnO layer on a *n*-type ZnO substrate[72]. A Zn-phosphide compound, used as a phosphorous source, was deposited on the ZnO wafer and subjected to excimer-laser pulses. But the authors indicate that an attempt to prove the *p*-type nature of the P-doped layer by Hall measurements was not successful. It has to be stressed that a highly damaged layer is generally found on surfaces as a result of laser annealing.

In a recent communication, hole carrier concentrations of 10^{18}-10^{21} cm^{-3}, associated with mobilities of 0.1-50 cm^2/Vs and resistivities of 10-10^{-5} Ωcm have been reported in ZnO layers grown by pulsed layer deposition on GaAs substrates[73]. The As atoms out-diffusing from the substrates into the ZnO layers were considered as the dopant elements. Their concentration were found to be in the range of upper 10^{17} to upper 10^{21} $atoms/cm^3$ from SIMS measurements. No diodes have been so far fabricated from such layers. Furthermore, the electrical characteristics are said to "may have large uncertainties because contributions from the interference layers between the ZnO film and the GaAs substrate are not understood very well at this moment". In similar heterostructures, but with a ZnSe layer instead of ZnO on GaAs substrates, a highly *p*-type conductivity has been reported in the past[74]. Raman spectroscopy measurements gave evidence of the presence of a *p*-type carrier gas with *p* ranging from 10^{18} to 10^{20} cm^{-3}, which appeared as confined at the interface of ZnSe/GaAs[75-77].

6. CONCLUSIONS

ZnO presents very attractive physical properties which have been reviewed and for some of them compared to those of GaN. As a result of these properties, the various applications which could be thought of for ZnO have been summarized. A critical review is then proposed of the different techniques used for the growth of bulk ZnO crystals and of ZnO epitaxial films. The results are discussed from the assessment of the structural and electrical properties of the crystals and films. Among the numerous communications related to the ZnO epitaxial growth, a very few of them report on layers of structural and electronic properties suitable for optoelectronic devices. *P*-type doping, discussed in the light of the most recent results, remains the key issue for the optoelectronic development of ZnO.

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